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Template-free synthesis of $Cu@Cu_2O$ core–shell microspheres and their application as copper-based catalysts for dimethyldichlorosilane synthesis

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HIGHLIGHTS

- ▶ $Cu@Cu_2O$ core–shell microspheres were prepared via a template-free solvothermal method.
- ▶ The effect of synthesis parameters on the morphology of products were investigated.
- ▶ The formation mechanism of $Cu@Cu_2O$ core–shell structure was tentatively proposed.
- ▶ $Cu@Cu_2O$ exhibited an enhanced catalytic activity for dimethyldichlorosilane synthesis.

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ABSTRACT

We report the synthesis of $Cu@Cu_2O$ core–shell microspheres via a facile template-free solvothermal method. The resulting products were characterized by X-ray diffraction, scanning electron microscopy with energy-dispersive spectroscopy, transmission electron microscopy, temperature-programmed reduction, and thermogravimetric analysis. It is found that, Cu_2O microspheres were firstly formed through the reduction of copper acetate by glutamic acid, and then, the reduction started inside the microspheres due to the higher surface energies of inner Cu_2O particles, resulting in the formation of $Cu@Cu_2O$ core–shell structure. The content of Cu core in the composite microspheres increased with the reaction time and temperature. The as-prepared $Cu@Cu_2O$ core–shell microspheres exhibited a better catalytic performance for dimethyldichlorosilane synthesis than pure Cu_2O and Cu, and even superior to the physically mixed Cu and Cu_2O microspheres possibly because of the synergistic catalytic effect. These $Cu@Cu_2O$ core–shell microspheres will have potential application in organosilicon industry as copper-based catalysts.

1. Introduction

Recently, there has been increasing interest in the controllable synthesis of core–shell inorganic micro/nanostructures because of their special geometries, unique properties [1–3], and wide applications [4,5]. It is reported that core–shell structures containing metal [6,7], polymer [8], semiconductor [9], inorganic material [10], metal oxide@C [11], and carbon/inorganic hybrid [12] have been synthesized and used in optics [13], pharmaceutics [14], semiconductor [15], catalysis [16], sensors [17], and Raman scattering [18]. Among various core–shell structures, the ones with metal core and metal oxide shell are of particular interest, as they can be used in CO gas absorption [19], magnetic [20], electronic [21], and catalytic applications [22,23]. One particular example is the Cu-core and its oxide-shell structures. In the last years, Cu/Cu_2O core–shell and hollow Cu_2O nanodendrites [18], mesoporous Cu/Cu_2O [24], Cu/Cu_2O cermets [25], $Cu–Cu_2O$ heterogeneous architectures [26], Cu/Cu_2O nanoparticles [27], $Cu@Cu_2O$ core–shell nanoparticles [19], Cu/Cu_2O hollow microspheres [28], and Cu/Cu_2O hollow nanocubes [29] have been synthesized using electrodeposition [18], co-deposition [19], milling method [25], two-step synthesis [29] with toxic reducing agent [27], respectively, because of the fact that copper (Cu) [30] and cuprous oxide (Cu_2O) [31,32] are widely used in catalysis. However, it still remains a big challenge to synthesize these core–shell nanostructures in a green way, thus developing facile, template-free, one-step process is highly desirable.

Since Rochow discovered the direct synthesis route to produce methylchlorosilanes (MCSs) using Si particles to react with gas chloromethane (MeCl) over the copper-based catalysts in 1940s [33], named Rochow reaction, this reaction is still the most economical route in organosilane industry for direct synthesis of methylchlorosilanes (MCSs) [34]. Metallic copper and its compounds including Cu_2O [35], CuO [36], CuCl [37], Cu_3Si [38], and

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